Title: Oxidation of starch

Background of the Invention

The invention relates to oxidized starch, the production thereof, as well as to the use of oxidized starch in various applications.

Oxidized starches have found many applications in industry. Examples of common applications include the use of oxidized starch in the paper industry, for instance in coatings or surface sizing, the adhesive industry, the textile industry, and the food industry.

The preparation of oxidized starches is conventionally carried out by oxidation with an alkali metal hypochlorite, which is a relatively cheap oxidizing agent.

The main factors controlling the oxidation reaction are the amount of alkali metal hypochlorite used, the pH, the temperature, and the use of metal and/or bromide ions as catalyst. An overview of the most important reaction parameters may be found in an article by J. Potze and P. Hiemstra in Starch, vol. 15, pp. 217-225 (1963). It has been proposed that dissociation of the hypochlorite in solution and the presence of radicals in the reaction mixture determine the reaction mechanism. Despite the extensive research done, the exact mechanism of the hypochlorite oxidation of starch is, however, still not entirely clarified.

As has been mentioned above, the course of the oxidation reaction using an alkali metal hypochlorite depends much on the pH during the reaction. This dependency has been widely addressed in the literature. The highest reaction rates are found at neutral pH, while the reaction rate decreases with increasing pH. At acidic pH (<5), chlorine is formed, which, for evident reasons, is to be avoided in an industrial process. Thus, from the view of the reaction rate, it would be desirable to perform the oxidation reaction at or around a neutral pH.

During the oxidation of starch with an alkali metal hypochlorite, different reactions occur. These reactions lead

to the introduction of carboxyl and carbonyl groups, and to
the degradation of the starch molecule. The course of all
these reactions, and the balance among them, determine the
properties of the oxidized starch that is obtained. The
balance among said reactions, i.e. the relative amount in the
oxidized starch of carboxyl and carbonyl groups and the
extent of degradation of the starch molecule, are, in their
turn, dependent on the pH during the oxidation reaction.
Hence, the properties of an oxidized starch will depend on
the pH at which the oxidation reaction is carried out.

The degradation of the starch molecule during
oxidation leads to a lower viscosity of a solution (or
dispersion) of the oxidized starch, which is usually desired
of an oxidized starch. It has been found that the degradation
occurs to a farther extent at neutral pH of about 7-7.5, than
at alkaline pH, such as pH 9 or higher. In other words, in
order to obtain an optimal yield of oxidized starch providing
a solution or dispersion of low viscosity, the oxidation
reaction should preferably be carried out at neutral pH.

However, the viscosity in solution (or dispersion) is
not the only important property of an oxidized starch. The
viscosity of said solution (or dispersion) is, for most
purposes, required to not, or hardly, fluctuate in time. The
viscosity of the solution (or dispersion) should remain
stable during storage.

Carboxyl groups, that may be introduced in the starch
during the oxidation reaction, provide the desired stability
of the viscosity of an oxidized starch solution or
dispersion. The higher number of carboxyl groups, the better
the viscosity stability. Contrary to the degradation of the
starch, the amount of carboxyl groups introduced in the
starch during oxidation with an alkali metal hypochlorite is
small when the oxidation is carried out at neutral pH. The pH
at which a high number of carboxyl groups is introduced lies
around 8.5.

Besides choosing the oxidation reaction conditions so that a high number of carboxyl groups are introduced, the stability of the viscosity of solutions (or dispersions) of oxidized starch may be increased by introducing ether or
5   ester groups in the starch. Examples of such groups include hydroxyethyl, hydroxypropyl and acetyl groups. Disadvantages of this route are that an additional derivatization step is needed, in which toxic reagents are used.

The number of carbonyl groups introduced in the
10   starch during oxidation negatively affects the stability of the viscosity of the oxidized starch in solution (or dispersion). It further leads to a more brown-yellow color of a solution or dispersion of the oxidized starch, which is usually not wanted. The amount of carbonyl groups introduced
15   is also dependent on the pH during the oxidation reaction. At neutral pH, a relatively high number of carbonyl groups is introduced. At a higher pH, less carbonyl groups will be introduced during oxidation.

From the above, it will be clear that the choice for
20   the pH at which conventional oxidation reactions of starch using an alkali metal hypochlorite are performed, constitutes a compromise between efficient starch degradation and stability of the viscosity of the oxidized starch when dissolved or dispersed. This compromise becomes even more
25   apparent from the data presented in the below table I.

Table I

	pH during oxidation		
	7.0 - 7.5	8.0 - 9.0	9.5 - 10.5
Degradation	+++	+	++
Carboxyl groups	+	+++	++
Carbonyl groups	+++	++	+

In table I, the number of +'s indicates the extent to
30   which the specific reaction occurs at a given pH.

Conventionally, the pH during oxidation of starch using an alkali metal hypochlorite is chosen at 8.5 or higher, dependent mostly on the desired viscosity of the oxidized starch.

5 The international patent application WO-A-97/04167 relates to the use of an amylopectin type starch, obtained from potato that has been modified by genetic engineering to suppress the formation of amylose-type starch, as a finishing agent in papermaking. The amylopectin type starch is

10 subjected to oxidation, enzymatic treatment, acid hydrolysis or thermo-chemical conversion. The disclosed oxidation process is performed at pH 9.5. According to the document, the obtained oxidation product may, as such, be used as a finishing agent in papermaking.

15 As has been indicated above, for reasons of stability, in particular viscosity stability, of the oxidized starch, the oxidation process is usually carried out at a pH higher than 8.5. However, the high pH adversely affects the reaction rate. Also, carrying out the oxidation process at

20 this pH has the effect that relatively high amounts of oxidizing agent are necessary to achieve the desired viscosity. As the oxidizing agent is usually an alkali metal hypochlorite, the more oxidizing agent is used, the higher the risk that a certain amount of chlorine ends up in the

25 oxidation product. The presence of chlorine is for evident reasons highly undesirable with respect to (public) health and the environment. *THE INVENTION*

SUMMARY OF The present invention aims to overcome the above problems. The invention further aims to provide a process for

30 the oxidation of starch wherein significantly less oxidizing agent is necessary than in the prior art processes. It is also an object of the invention to provide a process for the oxidation of starch wherein an oxidized starch is obtained, which has excellent properties, such as viscosity and

35 (viscosity) stability.

DETAILED DESCRIPTION OF THE INVENTION

Surprisingly, it has been found that the above objects are achieved by oxidizing a specific type of starch and by subjecting the oxidation product to an alkaline treatment. Thus, the invention relates to a process for the
5   oxidation of starch, wherein a root or tuber starch comprising at least 95 wt.% of amylopectin, based on dry substance of the starch, is treated with an oxidizing agent and the resulting product is subjected to an alkaline treatment, which treatment comprises keeping the product for
10 at least 15 minutes at a temperature of 20-50°C and a pH higher than 10.

It has been found that the oxidation of starch according to the invention requires only small amounts of oxidizing agent, while the obtained product has excellent
15 properties, in particular a very good viscosity stability. Furthermore, it has been found that, when an alkali metal hypochlorite is used as an oxidizing agent, much smaller amounts of chlorine are present in the obtained oxidized starch in comparison with prior art oxidized starches. In
20 addition, it has been found that the oxidation process can be carried out in a shorter period of time than the prior art oxidation processes.

As has been indicated above, according to the invention, a starch is oxidized, which starch has a very high
25 amylopectin content. Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of
30 polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch)
35 contain 15 to 30 wt.% amylose.

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Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch
5   granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin starch granules isolated
10 therefrom as waxy cereal starches.

In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato
15 tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry
20 substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the
25 granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being
30 prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the
35 GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of

amylose-free starch mutant of the potato (*Solanum tuberosum*
L.)", Theor. Appl. Gent., (1987), 75:217-221, and E. Jacobsen
et al., "Introduction of an amylose-free (amf) mutant into
breeding of cultivated potato, *Solanum tuberosum L.*,
5   Euphytica, (1991), 53:247-253.

Elimination or inhibition of the expression of the
GBSS gene in the potato is also possible by using so-called
antisense inhibition. This genetic modification of the potato
is described in R.G.F. Visser et al., "Inhibition of the
10   expression of the gene for granule-bound starch synthase in
potato by antisense constructs", Mol. Gen. Genet., (1991),
225:289-296.

By using genetic modification, it has been found
possible to cultivate and breed roots and tubers, for
15   instance potato, yam, or cassave (Patent South Africa
97/4383), of which the starch granules contain little or no
amylose. As referred to herein, amylopectin potato starch is
the potato starch granules isolated from potato tubers and
having an amylopectin content of at least 95 wt.% based on
20   dry substance.

Regarding production possibilities and properties,
there are significant differences between amylopectin potato
starch on the one hand, and the waxy cereal starches on the
other hand. This particularly applies to waxy maize starch,
25   which is commercially by far the most important waxy cereal
starch. The cultivation of waxy maize, suitable for the
production of waxy maize starch is not commercially feasible
in countries having a cold or temperate climate, such as The
Netherlands, Belgium, England, Germany, Poland, Sweden and
30   Denmark. The climate in these countries, however, is suitable
for the cultivation of potatoes. Tapioca starch, obtained
from cassave, may be produced in countries having a warm
climate, such as is found in regions of South East Asia and
South America.

35   The composition and properties of root and tuber
starch, such as amylopectin potato starch and amylopectin

tapioca starch, differ from those of the waxy cereal
starches. Amylopectin potato starch has a much lower content
of lipids and proteins than the waxy cereal starches.
Problems regarding odor and foaming, which, because of the
5   lipids and/or proteins, may occur when using waxy cereal
starch products (native and modified), do not occur, or occur
to a much lesser degree when using corresponding amylopectin
potato starch products. In contrast to the waxy cereal
starches, amylopectin potato starch contains chemically bound
10   phosphate groups. As a result, amylopectin potato starch
products in a dissolved state have a distinct polyelectrolyte
character.

        According to the present invention, the amylopectin
starch to be oxidized is a root or tuber starch. It has been
15   found that the presence of the lipids and proteins adversely
affects the oxidation reaction, leading to by-products
because of which the oxidized starch is not of sufficient
quality. Furthermore, the presence of lipids and proteins
leads to an unacceptably high AOX level, wherein the AOX
20   level is defined as the amount of material that adsorbs to
active carbon when the oxidized starch is brought into
contact with said active carbon. The AOX level provides an
indication of the amount of halogenic material, such as
chlorine, in the oxidized starch.

25   The oxidation of amylopectin potato starch and
amylopectin tapioca starch has been found to lead to
particularly advantageous oxidized starches.

        The oxidation of starch is, according to the
invention, carried out with an alkali metal hypochlorite as
30   oxidizing agent. Preferably, sodium hypochlorite is used as
as an oxidizing agent. Alkali metal hypochlorites are
relatively cheap and have a relatively large oxidizing power,
thus leading to a very efficient and fast oxidizing process.

        The amount in which the oxidizing agent is added may
35   vary between 0.001 and 0.4 moles of alkali metal hypochlorite
per mole starch, preferably between 0.0025 and 0.15 moles of

alkali metal hypochlorite per mole starch. The skilled person
will be aware that the alkali metal hypochlorite should be
added to the starch in a controlled manner. It is one of the
advantages of the invention that significantly smaller
amounts of oxidizing agent are sufficient, when compared to
prior art oxidation processes of starch, for preparing an
oxidized starch having the same viscosity.

In a preferred embodiment, the oxidation of starch is
performed at pH between 6 and 10, more preferably between 6.5
and 8.5, even more preferably between 7 and 8. It has been
found that by working at a pH in these ranges particularly
small amounts of oxidizing agent suffice in order to obtain
an oxidized starch having excellent properties. As has been
mentioned above, it is one of the advantages of the invention
that it is possible to perform the oxidation reaction at a
lower pH than in conventional processes, while a product
having the same viscosity, and an increased viscosity
stability, when in solution or dispersion is being prepared.

In order to maintain the pH at a desired value, it
may be necessary to add an acid or a base to the reaction
mixture. For this purpose, suitable acids and bases may be
chosen such that they have substantially no negative effect
on the oxidation reaction or on the oxidized starch.
Preferably, hydrochloric acid or sodium hydroxide is used.

A problem associated with the prior art processes for
oxidizing starch, when carried out at a pH below 8.5, is that
during dissolution of the granular oxidized starch in water,
at high temperature a very high peak viscosity is observed.
In fact, the viscosity may temporarily become so high, that
processing is no longer possible. This is an undesired
characteristic of oxidized starches, particularly when used
at high dry solid concentrations. Surprisingly, it has been
found that the problem of the viscosity peak during
dissolution does not, or only to an acceptable degree, occur
in a process according to the invention, even when the
oxidation reaction is carried out at a pH below 8.5.

The temperature at which the starch, in accordance
with the invention, is treated with an oxidizing agent is
preferably chosen between 20 and 50°C, more preferably
between 25 and 40°C.

5   The oxidation reaction may be carried out as a
suspension or solution reaction in water. Preferably, the
reaction is carried out as a suspension reaction in water, as
this leads to a granular oxidized starch. To this end, the
starch to be oxidized is suspended in water in an amount
10   ranging between 0.5 and 1.5 kg of dry starch per liter water.

        Optionally, a catalyst or a combination of catalysts
may be used in the oxidation reaction. Suitable catalysts
include bromide, cobalt, iron, manganese and copper salts.
The catalyst or catalysts will be applied in catalytic
15   amounts, which will be no higher than 10 wt.%, with respect
to the amount of alkali metal hypochlorite.

        An important aspect of the present invention, is that
the reaction product of the above described oxidation
reaction is subjected to an alkaline treatment. This
20   treatment comprises keeping the product for at least 15
minutes at a temperature of 20-50°C and a pH higher than 10.
Surprisingly, it has been found that the alkaline treatment
has a highly beneficial effect on the properties, especially
the viscosity stability, of the oxidized starch. An oxidized
25   starch according to the invention may be stored at increased
temperatures, e.g. 80°C, for prolonged periods of time
without substantially any change in the viscosity of the
product being observed.

        Preferably, the alkaline treatment lasts at least 30,
30   more preferably at least 60 minutes. Although there is no
critical upper limit for the duration of the alkaline
treatment, it will usually not be carried out for more than 6
hours in order to prevent that too much of the desired
product dissolves in the water. The pH at which the alkaline
35   treatment is carried out is preferably higher than 10.5.
Further preferred is that the pH is kept below 12. It has

been found that according to these preferred embodiments, an even higher viscosity stability may be achieved.

In view of the above mentioned increased viscosity stability of a solution or disperion of an oxidized starch prepared as disclosed hereinabove, it will be clear that the invention also relates to an oxidized starch obtainable by a method disclosed hereinabove.

It has been found that an oxidized starch prepared in a process according to the invention meets the following conditions:

$$(I.V. * ZGT)^{-1} \geq X, \text{ and}$$

$$BU_{top} / BU_{90-20} \leq Y,$$

wherein I.V. is the intrinsic viscosity of the oxidized starch;

ZGT is the acid number of the oxidized starch;

BU_{90-20} is the Brabender viscosity of the oxidized starch after being held for 20 minutes at 90°C, measured using the oxidized starch in a concentration resulting in a BU_{90-20} between 100 and 500 BU;

BU_{top} is the peak Brabender viscosity of the oxidized starch, measured at the same concentration as the BU_{90-20};

X is 0.015, preferably 0.017, more preferably 0.019; and

Y is 17, preferably 13, more preferably 10.

According to the invention, the intrinsic viscosity is expressed in dl/g, and may be determined in a known manner, for instance as described in H.W. Leach in Cereal Chemistry, vol. 40, page 595 (1963),using an Ubbelohde viscosity meter and a 1 M sodium hydroxide solution in water as the solvent.

The acid number (ZGT) provides an indication of the number of carboxyl groups present in the oxidized starch. It is defined as the amount in µg equivalent of NaOH which is necessary per gram of dry starch to obtain a pH of 8.6 (µg eq/g ds). The ZGT is determined titrimetrically. The starch is brought in its acid form with hydrochloric acid and titrated to a pH of 8.6 using 0.1 M NaOH.

In order to measure the BU_{top} and BE_{90-20}, a Brabender
viscograph is used to record a viscosity curve. The Brabender
viscosity is expressed in Brabender units (BU). The program
used in accordance with the invention to measure the two

5   parameters comprises a heating gradient of 1.5°C/min., a
rotation of 75 rpm, and a torque of 250 cmg, using a
suspension of the oxidized starch and water comprising 5 to
40 wt.% of dry starch. The suspension is heated from room
temperature to 90°C, and kept at that temperature for 20

10   minutes. The peak viscosity thus obtained is the BU_{top}. The
viscosity measured after 20 minutes at 90°C is the BU_{90-20}. The
concentration of the oxidized starch in the suspension
depends on the amount of alkali metal hypochlorite used
during oxidation. The concentration should be adjusted such

15   that a BU_{90-20} is obtained in the range of from 100 to 500 BU.
Of course, the concentration for measuring BU_{top} is equal to
that for measuring BU_{90-20}.

The invention further relates to the use of an
oxidized starch as described above in the paper, adhesive,

20   textile and food industries.

In the paper industry, oxidized starches have been
used as coating binders since 1903. The main purpose of
coating paper is to improve its printability. The most
important components of a coating (also referred to as

25   coating color) are pigments, such as titanium oxide, calcium
carbonate, clays, and the like, binders, such as latices,
starches, PVOH, proteins, and the like, and water.

In order to improve the quality of coated paper and
to reduce the energy consumption of drying the paper after

30   coating, the trend in the paper industry is to increase the
dry solids content of the coating colors. In a presentation
at the 18th PTS Coating Symposium 1997 in Munich, P.H.
Brouwer and B.C.A. ter Veer showed that low viscous starches,
such as oxidized starches, are excellent binders in such high

35   dry solids coatings.

In order to obtain a high dry solids coating, the
oxidized starch must be cooked at high concentrations (up to
40%) and stored in that concentration. This means that
storage of the starch solution takes place at high
5   temperatures (approximately 80°). As has been mentioned
above, the present oxidized starches have an excellent
viscosity stability, also at high temperatures. This makes
them highly suitable for use as a binder in paper coatings.

Another application of oxidized starches in the paper
10   industry concerns surface sizing, especially in the case of
high starches. In surface sizing, a solution of starch is
applied on paper. The concentration of the starch solution
generally lies between 2 and 20%, preferably between 5 and
12%.

15   Starches oxidized with relatively low quantities of
alkali metal hypochlorite are relatively high viscous
starches, having a relatively low amount of carboxyl groups.
Starches produced according to the prior art give starch
solutions which are not stable in viscosity, even at the low
20   concentrations used in surface sizing. Viscosity stability
has therefore to be introduced by chemical means, e.g. by
substitution of the starch with acetyl or hydroxy-alkyl
substituents. Oxidized starch prepared according to the
invention do not need such a modification to give solutions
25   of sufficiently stable viscosity. Thus, the present oxidized
starch is highly suitbale for replacing high viscous
hydrocolloids, such as polyvinyl aclohol, guar, alginate,
carboxymethylcellulose or hydroxyethylcellulose.

Yet another application wherein the present oxidized
30   starch has been found to be highly suitable is in adhesives.
The present oxidized starch may be used to adhere two or more
layers of paper together to form a multi-layer paper or
(card)board. Also, aluminum foil can suitably be adhered onto
paper by use of an oxidized starch according to the
35   invention. Further, the present oxidized starch may be used
as a component in paper sack adhesives and wall paper

adhesives, leading to an adhesive providing improved binding strength. In addition, paper and tape may be gummed with the present oxidized starch to produce stamps or envelopes. In abrasive paper or abrasive linen, the present oxidized starch
5   may be used to adhere abrasive particles, such as sand, onto the paper or linen. In addition, the present oxidized starch may be used as an adhesive for seeds or fertilizers.

Still another application is related to the stabilization of emulsions, in particular of emulsions used
10   in the adhesive industry such as polyvinylacetate emulsions. An oxidized starch according to the invention may be used as a protective colloid for providing the desired stability.

In the textile industry, the present oxidized starch may be used to improve the weaving operation or weaving
15   efficiency by warp yarn sizing. This results in an improved abrasion resistance of the warp yarns during the weaving process and less warp-end breakages. The present oxidized starch may further be applied as finishing agent to give a smooth and firm hand to fabrics. It may also be used for the
20   coating of glass fibers (fabrics and non-wovens). In addition, it may be used as blanket adhesive in the textile printing industry.

In the food industry, Arabic gum may be replaced in e.g. confectioneries by an oxidized starch according to the
25   invention. The excellent stability of the present oxidized starch, leads in these applications to a more clear food product.

It will be clear to the skilled person that the above list of applications is not intended to be extensive and that
30   many more applications of the present oxidized starches are conceivable. In practice, the present product may be used in any application in which oxidized starches have conventionally been used.

The invention will now be elucidated by the following
35   non-restrictive examples.

Example 1.

3.285 kg of amylopectine potato starch (2.83 kg dry matter)
was suspended in 3.98 kg of water. The temperature of the
5   suspension was increased to 35°C. 240 ml of a sodium
hypochlorite solution containing 146.5 g/liter of active
chlorine was added. During the oxidation the pH was
maintained at 7.5 by the addition of a 4.4 wt.% sodium
hydroxide solution. Once the reaction was complete, i.e. no
10   chlorine was detectable with potassium iodide-starch paper,
the pH was increased to 10.5 by the addition of a 4.4 wt.%
sodium hydroxide solution. After two hours of alkaline post-
treatment 7 ml sodium hypochlorite solution was added for
decoloration, followed after two minutes by 2 g of sodium
15   bisulphite. The reaction mixture was neutralized to pH 5.0 by
the addition of 10 N H_2SO_4, whereupon the product was
dewatered and washed before drying.

Example 2.

20

3.285 kg of amylopectine potato starch (2.83 kg dry matter)
was suspended in 3.98 kg of water. The temperature of the
suspension was increased to 35°C. 240 ml of a sodium
hypochlorite solution containing 146.5 g/liter of active
25   chlorine was added. During the oxidation the pH was
maintained at 7.5 by the addition of a 4.4 wt.% sodium
hydroxide solution. Once the reaction was complete, i.e. when
no chlorine was detectable with potassium iodide-starch
paper, the reaction mixture was neutralized to pH 5.0 by the
30   addition of 10 N H_2SO_4, whereupon the product was dewatered
and washed before drying.

Example 3.

35   3.285 kg of amylopectine potato starch (2.83 kg dry matter)
was suspended in 3.98 kg of water. The temperature of the

suspension was increased to 35°C. 240 ml of a sodium
hypochlorite solution containing 146.5 g/liter of active
chlorine was added. During the oxidation the pH was
maintained at 7.5 by the addition of a 4.4 wt.% sodium
5   hydroxide solution. Once the reaction was complete, i.e. when
no chlorine was detectable with potassium iodide-starch
paper, the pH was increased to 11.5 by the addition of a 4.4
% sodium hydroxide solution. After one hours of alkaline
post-treatment 7 ml a sodium hypochlorite solution was added
10   for decoloration, followed after two minutes by 2 g of sodium
bisulphite. The reaction mixture was neutralized to pH 5.0 by
the addition of 10 N H_2SO_4, whereupon the product was
dewatered and washed before drying.

15   Example 4. Comparative to example 2 of WO 97/04167

1.525 kg of amylopectine potato starch (1.30 kg dry matter)
was suspended in 1.798 kg of water. The temperature of the
suspension was increased to 35°C. The pH was increased to pH
20   9.5 by the addition of a 4.4 % sodium hydroxide solution.
225 ml of a sodium hypochlorite solution containing 146.5
g/liter of active chlorine was added. During the oxidation
the pH was maintained at 9.5 by the addition of a 4.4 wt.%
sodium hydroxide solution. Once the reaction was complete,
25   i.e. when no chlorine was detectable with potassium iodide-
starch paper, the reaction mixture was neutralized to pH 5.0
by the addition of 6 N HCl, whereupon the product was
dewatered and washed before drying.

30   Example 5.

1.525 kg of amylopectine potato starch (1.30 kg dry matter)
was suspended in 1.798 kg of water. The temperature of the
suspension was increased to 35 °C. The pH was increased to pH
35   9.5 by the addition of a 4.4 % sodium hydroxide solution.

225 ml of a sodium hypochlorite solution containing 146.5
g/liter of active chlorine was added. During the oxidation
the pH was maintained at 9.5 by the addition of a 4.4 wt.%
sodium hydroxide solution. Once the reaction was complete,
5   i.e. no chlorine was detectable with potassium iodide-starch
paper, the pH was increased to 10.5 by the addition of a 4.4
wt.% sodium hydroxide solution. After two hours of alkaline
post-treatment 5 ml a sodium hypochlorite solution was added
for decoloration, followed after two minutes by 2 g of sodium
10 bisulphite. The reaction mixture was neutralized to pH 5.0 by
the addition of 6 N HCl, whereupon the product was dewatered
and washed before drying.

Example 6. Comparative to example 1 of WO 97/04167

15

1.537 kg of regular potato starch (1.30 kg dry matter) was
suspended in 1.785 kg of water. The temperature of the
suspension was increased to 35°C. The pH was increased to pH
9.5 by the addition of a 4.4 wt.% sodium hydroxide solution.
20 476 ml of a sodium hypochlorite solution containing 146.5
g/liter of active chlorine was added. During the oxidation
the pH was maintained at 9.5 by the addition of a 4.4 wt.%
sodium hydroxide solution. Once the reaction was complete,
i.e. when no chlorine was detectable with potassium iodide-
25 starch paper, the reaction mixture was neutralized to pH 5.0
by the addition of 6 N HCl, whereupon the product was
dewatered and washed before drying.

Example 7.

30

1.537 kg of regular potato starch (1.30 kg dry matter) was
suspended in 1.785 kg of water. The temperature of the
suspension was increased to 35 °C. The pH was increased to pH
9.5 by the addition of a 4.4 % sodium hydroxide solution.
35 476 ml of a sodium hypochlorite solution containing 146.5
g/liter of active chlorine was added. During the oxidation

the pH was maintained at 9.5 by the addition of a 4.4 wt.%
sodium hydroxide solution. Once the reaction was complete,
i.e. when no chlorine was detectable with potassium iodide-
starch paper, the pH was increased to 10.5 by the addition of
5   a 4.4 wt.% sodium hydroxide solution. After two hours of
alkaline post-treatment 5 ml a sodium hypochlorite solution
was added for decoloration, followed after two minutes by 2 g
of sodium bisulphite. The reaction mixture was neutralized to
pH 5.0 by the addition of 6 N HCl, whereupon the product was
10   dewatered and washed before drying.

Example 8

The oxidized starch derivatives were dissolved in 30% (dry
15   matter) on a boiling waterbath with high speed stirring (600-
1200 rpm). After 30 minutes the solutions were stored at 80°C
and the viscosity was measured after 0, 1, 3 and 20 hours.
The results of the different oxidized starches is shown in
table II.

Table II

Oxidized starch for example no.	1	2	3	4	5	6	7
Starch	APS	APS	APS	APS	APS	PS	PS
amount of Cl_2/kg starch (g)	10	10	10	20.4	20.4	43.3	43.3
pH during oxidation	7.5	7.5	7.5	9.5	9.5	9.5	9.5
alkaline post-treatment	yes*	no	yes@	no	yes*	no	yes*
Brookfield viscosity (30%, 80°C, 30 rpm)							
0 hours	95	510	98	106	91	53	51
1 hour	102	370	100	108	94	57	51
3 hours	102	250	102	103	94	56	48
20 hours	94	68	92	75	75	37	35
pH (20 hours)	5.9	4.4	5.6	5.9	5.8	5.5	5.4
visc. 20 hours/0 hours	0.99	0.18	0.94	0.71	0.82	0.70	0.69

* pH 10.5 for 2 hours
@ pH 11.5 for 1 hour
5   APS = amylopectin potato starch
PS = regular potato starch

From the data presented in table II, it can be seen that the
starches prepared according to example 1 and 3 exhibited an
10   excellent viscosity stability at 80°C.

Example 9

Brabender viscosity curves were measured in 30 wt.% (dry
15   matter), with the following temperature program; start 30°C,
heating to 90°C (1.5°C/minute), 20 minutes at 90°C, cooling
to 30°C (1.5°C/minute). The peak viscosity and the viscosity
after 20 minutes at 90°C (in Brabender units, BU) of the
different starches is depicted in table II. Also the peak-
20   breakdown ratio, defined as the peak viscosity divided by the
viscosity after 20 minutes at 90°C, is presented in table
III.

Table III

Oxidized starch from example no.	1	2	3	4	5	6	7
Starch	APS	APS	APS	APS	APS	PS	PS
amount of Cl_2/kg starch (g)	10	10	10	20.4	20.4	43.3	43.3
pH during oxidation	7.5	7.5	7.5	9.5	9.5	9.5	9.5
alkaline post-treatment	yes*	no	yes@	no	yes*	no	yes*
Brabender viscosity (30 wt.%, 250 cmg, 75 rpm)							
BU_{top}	730	##	700	2030	1430	1750	1180
BU_{90-20}	180	##	180	100	100	175	150
BU_{top}/BU_{90-20}	4.0	##	3.9	20	14	10	7.9

* pH 10.5 for 2 hours

@ pH 11.5 for 1 hour

5 ## to high peak viscosity to measure in Brabender at 30%

APS = amylopectin potato starch

PS = regular potato starch

It can be seen, that the products prepared according to

10 example 1 and 3 exhibited a peak-breakdown ratio of less then

5.

Example 10

15 The oxidized starch derivatives were analyzed for their
intrinsic viscosity (IV) and the acid number (ZGT). The
intrinsic viscosity was determined using an Ubbelohde
viscosity meter with 1 M NaOH as solvent. The acid number was
determined titrimetrically by bringing the starch in the acid

20 form using hydrochloric acid and by titrating to pH 8.6 using
0.1 M NaOH.
The results for the different oxidized starches are shown in
table IV.

Table IV

Oxidized starch from example no.	1	2	3	4	5	6	7
Starch	APS	APS	APS	APS	APS	PS	PS
amount of Cl$_2$/kg starch (g)	10	10	10	20.4	20.4	43.3	43.3
pH during oxidation	7.5	7.5	7.5	9.5	9.5	9.5	9.5
alkaline post-treatment	yes*	no	yes@	no	yes*	no	yes*
Analytic data							
IV (g/dl)	0.40	0.39	0.40	0.39	0.40	0.35	0.28
ZGT (µg eq/g ds)	113	115	113	179	175	324	312
(IV*ZGT)$^{-1}$	0.022	0.022	0.022	0.014	0.014	0.009	0.011

* pH 10.5 for 2 hours

@ pH 11.5 for 1 hour

5   APS = amylopectin potato starch

PS = regular potato starch

Example 11

10   The oxidized amylopectin starch, prepared in accordance with
Example 1, was tested in a wood containing topcoat in
comparison with carboxymethylcellulose (CMC). The coating
formula is depicted in Table V. The coating colors were
analyzed for their dry substance (CEM lab wave 9000), pH,
15   high shear viscosity (Hercules), Water retention (AAGWR) at
0.5 and 1.5 bar for 15 seconds and the viscosity established
by Eklund Capillary Viscometer (ECV).

Table V

Coating formula no.	I	II	
Premier No. 1 (ECC)	50	50	parts
Hydrocarb 90 (Omya)	50	50	parts
DOW 935	12	12	parts
Nopcote 104	0.9	0.9	parts
Oxidized starch		1.4	parts
CMC (Finnfix FF 30)	0.7		parts
Analyses:			
Dry substance	65.7	66.1	%
pH	8.8	8.8	
Brookfield viscosity 10 rpm	7600	4000	mPas
Brookfield viscosity 100 rpm	1320	840	mPas
High shear viscosity 100 rpm	191	162	mPas
High shear viscosity 1000 rpm	72.6	84.9	mPas
AAGWR 0.5 bar 15"	35.5	25.88	g/m^2
AAGWR 1.5 bar 15"	53.75	36.25	g/m^2
ECV 100000	120	89	mPas
ECV 700000	37	47	mPas

The rheological results indicate that a 2 to 1 replacement of CMC with oxidized amylopectin starch is possible, without a dramatic change in dewatering behavior.

5   Example 12

The oxidized amylopectin starch, prepared in accordance with Example 1, was tested in surface sizing in comparison with a commercial available oxidized and stabilized starch for ink-
10   jet printing paper. The ink-jet papers were analyzed for their sheet weight (Tappi T 140), starch content (Böhringer method), brightness (Tappi T 452), porosity (ISO 5636-5), HP ink-jet printability test (HP Paper Acceptance Criteria 3.4), bursting strength (Tappi T 405), stiffness (Tappi T 535),
15   tearing resistance (Tappi T 414), Internal bond (Tappi 506-wd-83/UM 584), Cobb test (NEN 3291), density ink-jet colors (Macbeth densito meter), Dennison wax test (Tappi T 459 SU-65) and the IGT pick resistance (Tappi T 514). The results are depicted in Table VI.

Table VI

Surface sizing formula no.	Regular starch	Amylopectin	
Density ink-jet colors			
black	0.83	0.93	
yellow	1.05	1.09	
magenta	1.02	1.09	
blue	1.31	1.32	
Internal bond	290	366	J/m^2
Stiffness	0.43	0.43	mN/m
Porosity	20.5	25.5	s/100 ml
Sheet weight	79.3	79.4	g/m^2
Tearing resistance	526	492	mN
Starch content	38	34	mg/g
Bleed	acceptable	acceptable	
Dennison wax test	16	16	
Cobb 60	19.1	17.3	g/m^2
Burst	171.3	156.2	kPa
Whiteness	87.32	86.68	%
Whiteness (UV)	99.96	98.37	%

Surface sizing with oxidized amylopectin starch resulted in a better ink-jet printability, higher internal strength, lower porosity and a lower Cobb 60 value. All these properties were obtained with a lower starch content of the paper.